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Porous silicon in solar cell structures: a review of achievements and modern directions of further use

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Abstract

Porous silicon, which is being obtained by electrochemical etching of silicon wafers in electrolytes on the base of hydrofluoric acid, recently attracted the attention of specialists in photovoltaics even more due to a number of its unique properties. However, at present, acceptable results are obtained for the use of porous silicon as antireflecting coating for silicon solar cells only. In the present paper, previous experience of the use of por-Si in the silicon solar cells has been reviewed. On the base of examination of the porous silicon properties, a number of new directions of improvement of photoconversion efficiency of structures with optimized layers of porous silicon are proposed. The results of numerical calculations carried confirm perspectiveness of use of porous silicon for efficiency improvement for different types of silicon solar cells. These can be increased of their internal quantum efficiency, expansions of operating spectral range toward ultra-violet and infrared spectrum range, decrease of losses of photogenerated power due to the influence of bulk and surface recombination. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction and historical perspectives

Presently, high costs are the main obstacles for a world-wide increase for

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utilization of electric power provided by photovoltaic solar cells (SC). Mass production can considerably reduce the price of SC, however, it is sufficient to reach the cost level necessary to become fully competitive with the conventional energy sources. Record laboratory efficiencies of 24% were obtained for single-crystal silicon SC with diffused p–n junctions [1–5]. However, they used extremely complex processing. It included surface structuring—inverted pyramids—by photolithography and etching, high temperature passivation by thermal oxidation, and the contact system has to be formed again by photolithography. It is clear that such fabrication process may not be suitable for a cost-effective mass production of SC.

It is necessary to note that if there are other directions of increase of photoconversion efficiency and reduction of manufacturing cost of SC, they will probably be connected with certain new materials and with some new effects, which traditionally were not used for photoconversion. Porous silicon (por-Si) is one of the materials, which have many unique properties for photovoltaic application as well as technological manufacturing simplicity.

Por-Si as a material of semiconductor electronics has been known since 1956 [6]. Its active structural and optical research began in 1990 from the discovery of intensive room-temperature photo- [7] and electroluminescence [8] in the visible

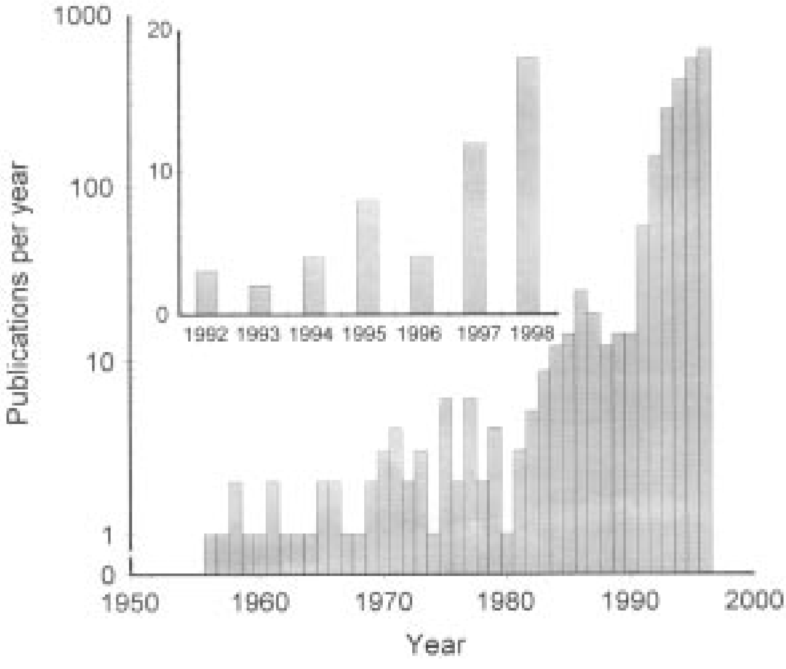

Fig. 1. Interest in por-Si: the histogram presents the total number of publications (archival journals and conference proceedings) per year since the discovery of the material to 1997 (from Ref. [9]). On the insert the total number of publications on photovoltaic application of por-Si is submitted.

spectrum. Much of the subsequent scientific research on por-Si (Fig. 1) [9] was directed toward determination of the light emission mechanism. This is not only a fundamentally interesting question, but it also has a direct influence on the usefulness of the material in integrated optoelectronics applications on silicon technology base [10].

It is not necessary to limit the application of por-Si with integrated optoelectronics scope. However, due to them, it could be one of the most perspective materials for optoelectronics devices using a photovoltaic effect. Insufficient quantity of experimental material, and also unsuccessful first attempts of fabrication of SC structures with por-Si were time barriers of extensive research in this direction. Nevertheless, the work quantity of photovoltaic using of the por-Si is growing constantly (Fig. 1). It evidently testifies that the given material should be considered as a new material of a silicon photovoltaics.

The purpose of the present paper is justification of efficiency of por-Si layers use in silicon SC structures on the base of study of microstructure and properties of this material, analysis of existed practice and engineering of new perspective ways of photovoltaic use of it.

2. Microstructure and properties of Por-Si

2.1. Por-Si formation

The formation of the por-Si films is realized mainly by means of electrochemical anodic treatment of silicon wafers in aqueous or alcohol electrolytes on the base of hydrofluoric acid of typical concentration from 20 to 50% (see the review [11]). The silicon here is an anode and the density of current passing through it (varies typically from 1 to 100 mA/cm^2 at the time from 1 to 60 min) should be less than certain critical value. This critical value is determined by concentration and viscosity of electrolyte, geometry of anode as well as physical properties of the silicon–electrolyte interface. Dimensions and type of conductivity of the original semi-conductor substrate, the value of anodic current and time of anodization influence characteristic dimensions of the microstructure, thickness of porous layer and other parameters of the material.

The por-Si formation mechanism has been studied for a long time [12]. The oxidation and dissolution re-actions of silicon with intermediate formation of a dioxide and bifluoride of silicon proceed parallel on a silicon surface during an electrochemical anodization. The majority of the offered models confirm it. Probably these reactions pass simultaneously and compete among themselves on speed. So it is supposed in the majority of works. The velocity of electrochemical reactions is also non-uniform on a silicon surface. Certain sites of a silicon surface, where the reactions proceed slower, will be etched less in comparison with sites where the reactions proceed faster. The dissolution heterogeneity of a silicon surface is a condition of por-Si formation [13]. However, such qualitative explanation of the por-Si formation mechanism cannot explain the process of

pores nucleation and their growth at the beginning of anode polarization of the silicon safer surface in HF-based electrolytes [12]. The pores initiation models offered today have some disagreement among themselves. The mathematical explanation of pores growth as a consequence of flat surface instability of silicon to small perturbations is offered in Ref. [14]. Some models connect the pores nucleating with near-surface vacancy supersaturation [15] or with microdefects etching, created as a consequence of a hydrogen surface supersaturation [16]. The

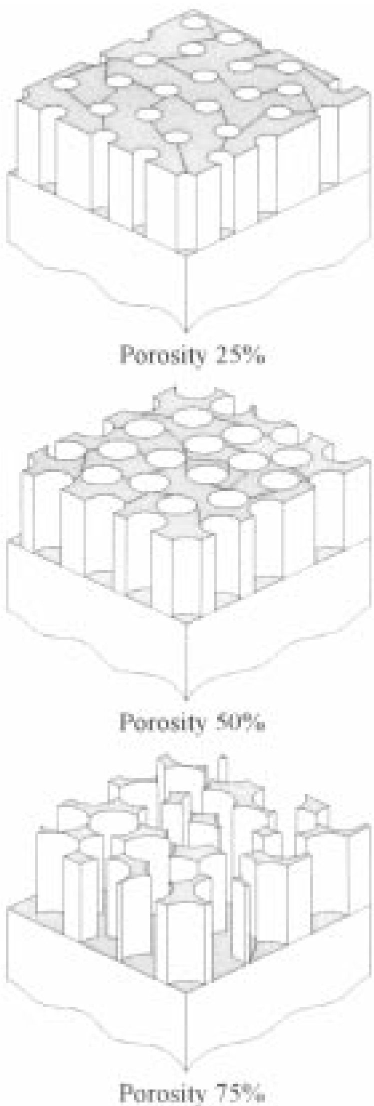

Fig. 2. Ideal model of porous silicon structure with different porosity.

silicon surface condition is a primary factor during a pores initiation both in first and in the second case.

2.2. Por-Si microstructure

Study of structure, made by different methods of electron microscopy [17] and energy dispersive X-ray (EDX) [18], shows that the por-Si has a crystal structure with a greater or smaller share of an amorphous phase [19]. The crystal lattice of original silicon remains unchanged but it is somewhat expanded [20], and filled with grid or pores and cavities, on the walls of which amorphous silicon precipitates. Under visual inspection the face of por-Si is smooth and mirror-like. State of porous silicon is characterized by a parameter called 'porosity', i.e. the ratio of empty volume (volume of the pores) to the total volume of the sample porous layer, as well as the average size of the microstructure elements.

The pore form, depending on crystallographic orientation of a silicon wafer, and also the type and quantity of a dopant, can be column type or represent a structure such as a coral or sponge type [21–23]. As a rule, the pores are oriented mainly along the (100) direction and their diameter (d_{por}) on surface of the received film can change from nanometric up to submicron size. Depending on a size range of pores, the following classification of por-Si layers [9] is accepted: microporous (d_{por} < 2 nm), mesoporous (2 < d_{por} < 50 nm) and macroporous

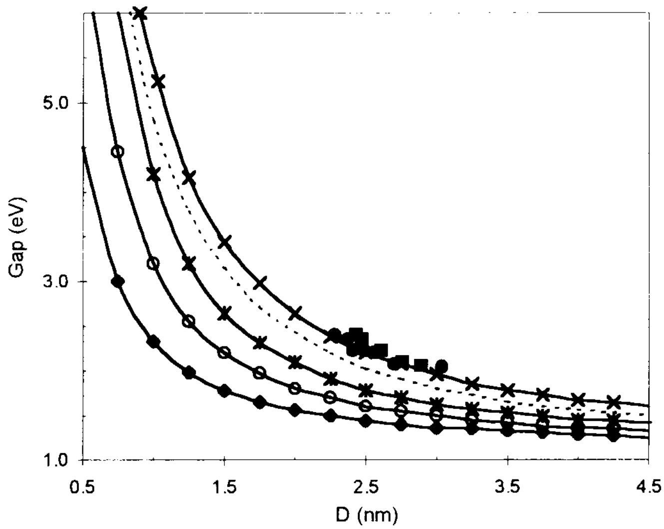

Fig. 3. Calculated optical band gap energies for various silicon crystallites (×) and wires ((100), *; (110), ◆; (111), ○) with respect to their diameter *d*. The full curves are an interpolation and an extrapolation of these results by d^{-n} law. The full circles and squares are the experimental results of Ref. [28]. The broken curve is the band gap energy for the crystallites including the coulombic interaction between the electron and hole. (from. Ref. [29]).

($d_{por} > 50$ nm). The por-Si layers thickness and porosity can be from the 100-th shares of a micron up to hundreds microns and from 30 up to 95% accordingly.

The pores merge among themselves with the increase of porosity (Fig. 2). forming columns of single-crystal silicon of diameter of order 2–5 nm [23]. These silicon columns, which later received the name 'quantum wires' [7], consist, in turn, of spherical or other form silicon clusters of nanometric size [23,24]. As it was shown in some theoretical papers [25,26], the energy gap of por-Si, being changed typically from 1.5 to 1.8 eV [27], is a function of the quantum wire diameter (Fig. 3). By the theory of quantum confinement of carriers in silicon wire volume, this question can be illustrated [7,27]. The silicon wire diameter depends on conditions of por-Si technology and its subsequent processings. Therefore there is a unique opportunity effectively to operate the band gap of this material by a technological way. It is justified theoretically, that just due to formation of quantum wires, transformation of the energy spectrum of single-crystal Si takes place and it converts from indirect bandgap semiconductor into the direct bandgap one [25]. This can explain high emittance of por-Si typical first of all for semiconductors with direct energy gap.

2.3. Chemical composition and electrical properties of por-Si

Analysis of extensive experimental material [30–34] in field of the por-Si chemical composition study shows that the only chemical elements on the surface of this material are Si, H, O and F. These results are confirmed also by secondary ion mass-spectroscopy (SIMS) [7] and X-ray photoelectron spectroscopy [35]. Studies by the method of SIMS have shown that on the broadly developed surface of por-Si there are the rests of electrolyte in form of ions OH^-, F^-, H^+, and shown that on the broadly developed surface of por-Si there are the rests of electrolyte in form of ions OH^-, F^-, H^+, and the compound components on the surface of the wires. They can be polysilanes, siloxenes with the different contents of oxygen, hydroxyl groups, hydrogen and oxides (Si_2O, SiO, SiO_2, SiOH, SiH, SiF, O^-, H^+, OH^-). Concentration of these compounds is various for different distances from the surface of the layer. Thus, the interval of distances 500–1500 Å is heavily enriched with hydrogen and OH^- groups.

The atoms of H and O are adsorbed on internal surfaces of pores as compounds Si–H and Si–O–Si, as follows from IR absorption spectra [36]. At that, the atoms F will be adsorbed without chemical interaction with Si. The X-ray photoelectron spectra allow to identify precisely the presence the SiO_2 thin layer with F impurity on the por-Si surface. As a result, the structure of near-surface region represents a mixture of Si:O:F atoms in the certain parity, e.g. 2:1:0.2 [37].

Among electric characteristics of the por-Si, the study of resistivity and photoconductivity is the most interesting problem for photovoltaic application. The specific resistance of the por-Si layers demonstrates its abnormal high value (10^6–10^7 Ωcm). It is close to specific resistance of the intrinsic silicon [38].

However, the layers of por-Si on the p-type Si wafers [39] had significant photoconductivity in visible range of spectrum despite their high dark resistance.

The study of electrical properties of the por-Si/Si structures [40] has revealed rectifying properties of this heterojunction. The space charge region (SCR) arises as a consequence of the fact, that the potential of a silicon wafer is positive in comparison with the porous layer potential. However, high imperfection of the por-Si layers causes low life times and diffusion lengths of photogenerated carriers and it is the reason of such low (~1%) value of collection efficiency in structures with the same type heterojunction [41].

3. Por-Si photovoltaic application

For the first time, considerable capacity of por-Si as the material for a silicon photovoltaics was noted in papers [42–44]. Herein, the following ways and advantages of por-Si photovoltaic application were formulated, proceeding from the analysis of microstructure and properties of this material:

1. The surface of the PS is highly texturized, which enhances light trapping and reduces reflection losses. It can be used for creation of antireflecting coatings for silicon SC.
2. The possibility of technological control of band-gap of por-Si (from 1.5 up to 1.8 eV) may be utilized to optimize sunlight absorption. In second, its wide bandgap may make it a candidate for the window layer in a heterojunction cell or as the base material for the top cell in a tandem construction. The wide bandgap may also be used to realise front or rear surface in a diffusion junction silicon SC.
3. Por-Si can be used for solar light transformation from an ultraviolet range (thanks to it's luminescent properties) in more long wavelength range, it's optimum for photovoltaic conversion in silicon SC.
4. The por-Si developed surface alongside with its high chemical activity can serve for effective impurity gettering in silicon SC substrates.
5. The simplicity of por-Si technological formation and using of its electrochemical growth technology on silicon large area wafers particularly appealing for SC cheap fabrication.

To the present time practical approbation in the photovoltaic application field have passed only the first and second points of the unique properties por-Si considered above. It is possible to explain this phenomenon only considering the problems, which arise on a way of inclusion the por-Si to SC structure [1]. At first, this is a por-Si high specific resistance, which limits an effective carriers transport in a material volume. Secondly, there is insufficient understanding of the mechanism of generation and collection of photogenerated carriers in por-Si. It prevents the creation of a high-efficiency SC design on its basis. Thirdly, it is a low mechanical strength of por-Si layers (especially with a high porosity) and also their insufficient thermal conductivity and high sensitivity to high-temperature

processing. It actually is a problem of stability of this material during SC fabrication.

The detailed consideration and experience analysis of por-Si utilization in silicon SC structures is given further. The special attention to positive results achieved in this area, is given. Thus their physical interpretation based on a known experimental material about the nature and properties of por-Si also is considered separate.

3.1. Antireflecting coating on por-Si base

For the first time the attention of the photovoltaic specialists was concentrated on por-Si in 80 years thanking its porous nature of a rough surface, low refractive index and blue shift of fundamental absorption edge (Fig. 4) [45]. These properties of por-Si assumed its availability as a material of an antireflecting coating for silicon SC.

The first experimental researches in this direction were carried out by Prasad et al. [46]. The authors of this paper used the por-Si layer for reflection reduction of polycrystalline SC with diffusion p^{+}-n junction by depth ~0.6 μm. Conventional electrochemical anodization for por-Si layer formation was not used. It was a method of photostimulated chemical etching. Thus the por-Si growth in the HF-based electrolyte take due to a course of a photocurrent, induced in structure with p–n junction by electrical illumination. A porous film thickness supervised on changing its interference colour. It might be typically 74 ± 2 nm. Ellipsometric

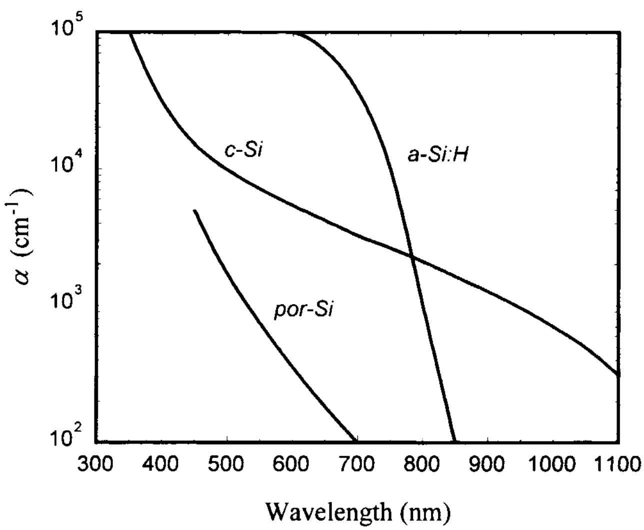

Fig. 4. Optical absorption coefficient versus wavelength for self-supporting 20 μm thick por-Si layer. Data for crystalline Si and amorphous Si:H is also shown. (from Ref. [45]).

measurements determined the refractive index of the por-Si layer. It was in a range 1.95 ± 0.05.

Such thin frontal layer of the por-Si in the silicon SC structure reduces its optical losses from 37 to 8% (Fig. 5) and increases a short-circuit current by 25% and open-circuit voltage by 20 mV, as experimental researches have shown. If the nonreflecting properties can explain such essential increase of a photocurrent, the gain of a SC output voltage is a result of a passivation by the por-Si layer of a silicon surface and as a consequence a reduction of a saturation current. The por-Si antireflecting coating insignificantly influences on the form of the current-voltage characteristic of SC (Fig. 5). Thus such characteristics as the fill factor, series and shunting resistance essentially did not vary. It is important that the por-Si antireflecting coatings have demonstrated the weatherproof fact during several months.

The researching of por-Si based antireflecting coverings was continued in papers [43–44] after more than ten years interruption. At that por-Si layer was formed on a surface of single-crystal silicon wafers by an electrochemical anodization and its thickness about 10 μm. The integrated reflectance of such nonreflecting coating changes from 1.6 to 3.4% in a spectral range from 400 to 900 nm have shown measurements of optical losses. The received results are compared on efficiency with the best antireflecting coatings of the double MgF_2/ZnS layer on the basis put on a texturized previously silicon surface [1]. At the same time, if similar por-Si layer to use on a substrate surface of polycrystalline silicon, the integrated reflective ability decreases only up to 10% for light waves with length from 400 to 900 nm [44].

The antireflecting coating in SC structure with dot contact has given effect of increase efficiency in consequence of optical losses minimization. But this effect

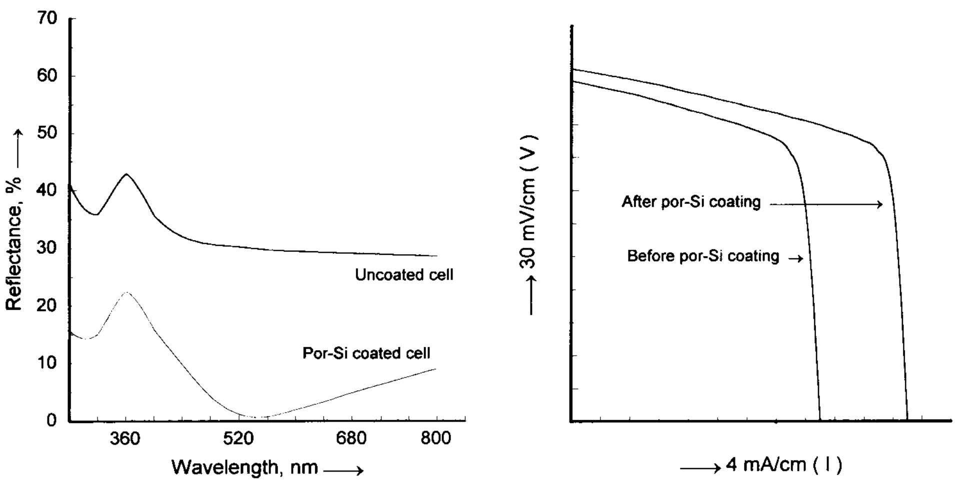

Fig. 5. Spectral reflectance and illuminated I–V characteristics of polycrystalline solar cells with and without por-Si coating (from Ref. [46]).

was accompanied by a degradation of an open-circuit voltage and short-circuit current in time [44].

The detailed study of por-Si layers antireflecting properties received by chemical etching in HF/HNO_3 based solution is carried out in paper [1]. The attention to this por-Si formation method the authors explain by its simplicity and cheapness in comparison by electrochemical anodization process. The concentration of oxidizing species in the chemical etching process seems to play the same role that the anodic current density plays in the electrochemical anodization process [1]. Polycrystalline silicon wafers by a boron doping was used as a substrate for por-Si layer formation.

Dependence of porous layer reflectance of its porosity in this paper at first is investigated as por-Si parameter optimization necessity for its using as silicon SC antireflecting coating. It was established that the lowest coefficient of por-Si reflection is reached with its porosity about 70% (Fig. 6). Thickness optimization of an antireflecting coating was carried out as porous layer surface optical reflection minimization. The integrated reflectance of por-Si layer a little bit depends from a type and doping degree of an initial polycrystalline substrate was established eventually and it changes in a spectral range 350–1120 nm from 4.7 to 4.9% (Fig. 7).

The further researches [47–49] of silicon SC with por-Si frontal layer have confirmed its antireflecting properties, but essential increase of a photoconversion efficiency could not demonstrate in consequence of the unoptimized structure of a

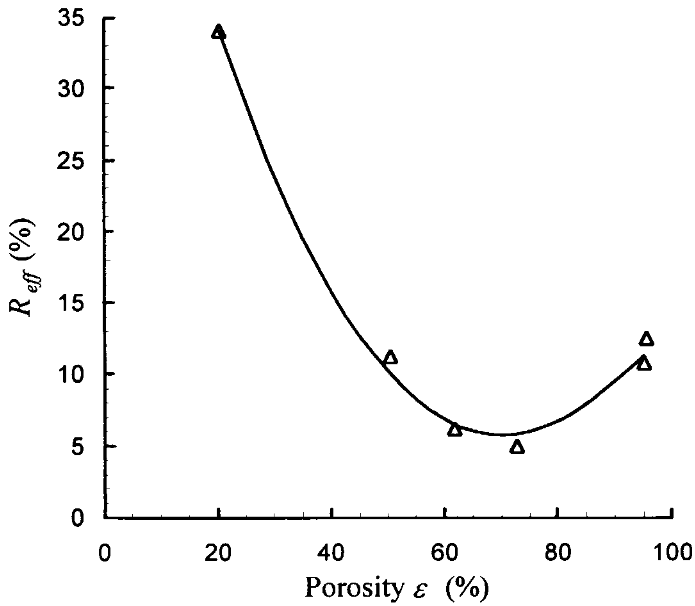

Fig. 6. Effective reflectance coefficient as a function of ϵ, the measured porosity of the por-Si layers. (from Ref. [1]).

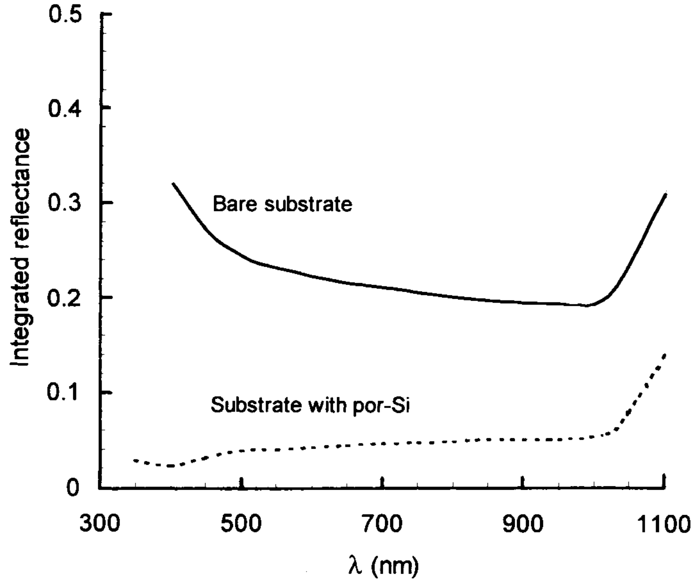

Fig. 7. Integrated reflectance of a por-Si layer formed on a p-doped, 1 Ωcm, as cut, polycrystalline wafer (Wacker, SILSO). The reflectance of bare substrate is also shown (from Ref. [1]).

SC. The results of subsequent papers [50–52] were more successful. The result of paper [52] was the SC with the 5×5 cm^2 area. Por-Si layer on its frontal surface was received by chemical etching in solutions with controllable composition. Efficiency of this SC under lighting AM 1.5 was 14.1%. However its spectral sensitivity, extended in infra-red range, and high quality of a surface passivation testify to a potential opportunity of the further increase of the output characteristics of this type of SC.

The paper [53] has presented the most wide-ranging and productive researches of influence of a thin frontal por-Si layer on photoelectric properties of the multicrystalline SC. The parameter optimization of a porous layer as for optical losses minimization on a reflection, as for achievement of the maximum of the output characteristics SC was its purpose. These two directions incompatible among themselves, but even in some cases are opposite on technological realization for the first time was shown. This conclusion is based on the fact that the increase of por-Si layer thickness which is necessary for optical losses decreasing simultaneously conducts to increase of series resistance of structure SC and lowers its fill factor. This was illustrated most clearly in [53] by the dependence of output parameters of SC on the charge value passed through the device structure during process of the por-Si layer formation (Fig. 8). As it follows from Fig. 8, there is certain value of the charge (and, consequently, thickness of the porous layer), when the output electrical characteristics begin to decrease sharply at exceedance of it. This means, that to reach maximal positive effect from

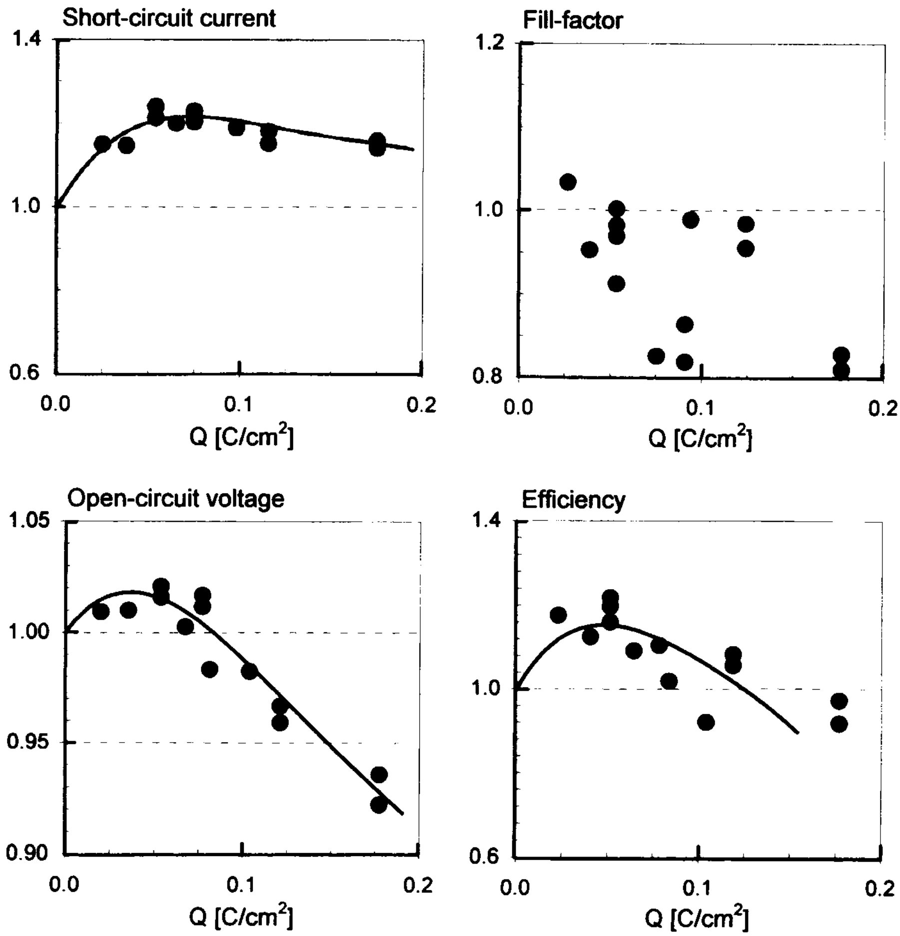

Fig. 8. Multicrystalline solar cell parameters as a function of the electrical charge passed through the cell during anodization. The data are normalised to the values before anodization (from Ref. [53]).

the use of antireflective por-Si layer in the structure of SC is possible only under detailed optimisation of its parameters.

According to the results of paper [53] the optimal parameters of the por-Si-based antireflecting coating for multicrystalline SC studied with shallow (~0.4 μm) n^+–p junction are the following: thickness 80 nm, porosity 69%, refraction index 1.64. The use of such optimised por-Si layer in structure of SC has allowed to increase the short-circuit current of the SC more than by 20% and improve the efficiency from 7.5–8.5 to 10–11%. The increase of photoresponse of the por-Si/ n^+-multi-Si/p- multi-Si structures (Fig. 9) observed in this case the authors of [53] relate not only to the reflection losses reduction, but to decrease of surface recombination by hydrogen covering of the por-Si surface as well.

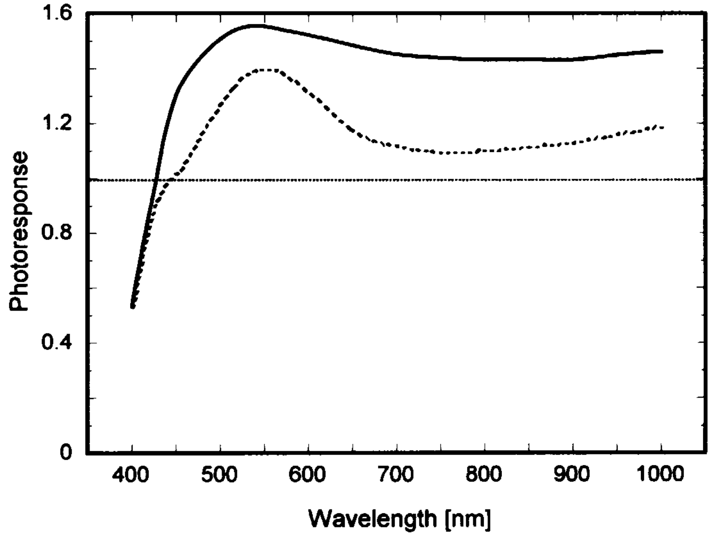

Fig. 9. Photoresponse spectra after etching. Normalised to the values before anodization. The two curves correspond to two different 2×2 mm^2 positions within the cell (from Ref. [53]).

The final confirmation of passivating influence of por-Si layer was obtained by Pačebutas et al. in their subsequent paper [54]. Considerable increase of photocurrent decay time induced in subsurface region of pre-anodized samples compare to samples not subjected to anodization was found by means of transient photoconductivity measurements.

Besides, in paper [54] they found strong dependence of optical properties of por-Si layer on conditions and length of electrochemical formation of it. To describe this dependence the authors set forth generalised criterion—value of charge passed through electrolyte during anodization. Although this parameter is not universal, the use of it is convenient enough to describe the dependence given. Thus, the result of short anodic etching (value of charge passed less than 0.3 C/cm^2) will be thin (~100 nm) nanoporous layer, which is the most effective for the use as antireflecting coating. The minimal reflectivity for multicrystalline SC with n^+–p junction is reached by anodization with the charge value of ~0.05–0.09 C/cm^2. This allows to increase the efficiency of these devices with area 10 cm^2 by 30% under AM 1.5 illumination [54].

The por-Si obtained after long electrochemical etching with anodization charge exceeding 10 C/cm^2 will be an array of the upper (~1–2 μm) nanoporous layer and lower microporous layer of several tens of μm thick with sizes of structural elements from hundreds of nanometers to several microns. Such coarse, sponge-like topology of microporous layer can be used for texturing of the SC surface, provided that the por-Si layer will have inhomogeneities proportional to the light wave length [54–57].

The effect of surface texturing by long anodic etching for the first time was

demonstrated in papers [54,55]. The measurements of optical transmission carried on silicon wafers of n-type with thick porous layer have fixed considerable reduction of the transmission value in wide spectral range (Fig. 10). This phenomenon was explained by isotropic distribution of photons inside of substrate with coarse texturized surface, in consequence of which many of the photons appear trapped and increase amount of absorbed light flux.

It is natural that the trapping effect should be the most considerable in long wavelength range of spectrum, the photons of which can not be absorbed effectively by silicon one pass through the substrate. This was confirmed experimentally in [54] by comparison of spectral photosensitivity of silicon wafers polished and texturized by anodization. The results obtained are presented in Fig. 11. They give the demonstrative evidence in favor of efficiency of use of thick microporous por-Si layers for expansion of spectral sensitivity of silicon SC in the band-edge absorption range.

The largest effect from the use of por-Si-based antireflecting coating was obtained by Vitanov et al. [58]. In this paper the influence of thickness of the por-Si frontal layer on output performance of the silicon SC with deep (2.2 μm) n^+–p junction have been studied. It is found that short-circuit current is the most sensible to variation of the por-Si layer thickness while open-circuit voltage and fill factor suffer minor changes (Fig. 12). As it follows from Fig. 12, maximal increase of photocurrent (more than by 50%) and output voltage (by ~5%) for the SC with por-Si/n^+–Si/p-Si structure can be obtained at the porous layer thickness of about 72 nm. At the same time, measurement of reflectivity of such

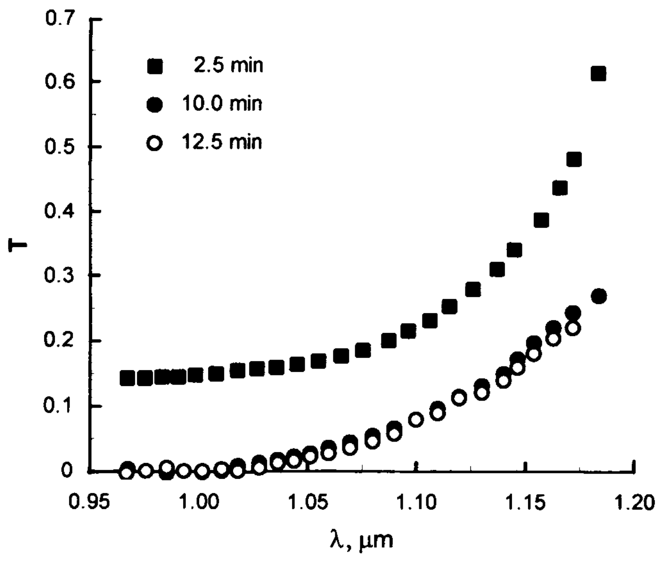

Fig. 10. Spectral dependencies of the relative transmittivity of silicon wafers covered with por-Si layer for different anodical etching durations (from Ref. [54]).

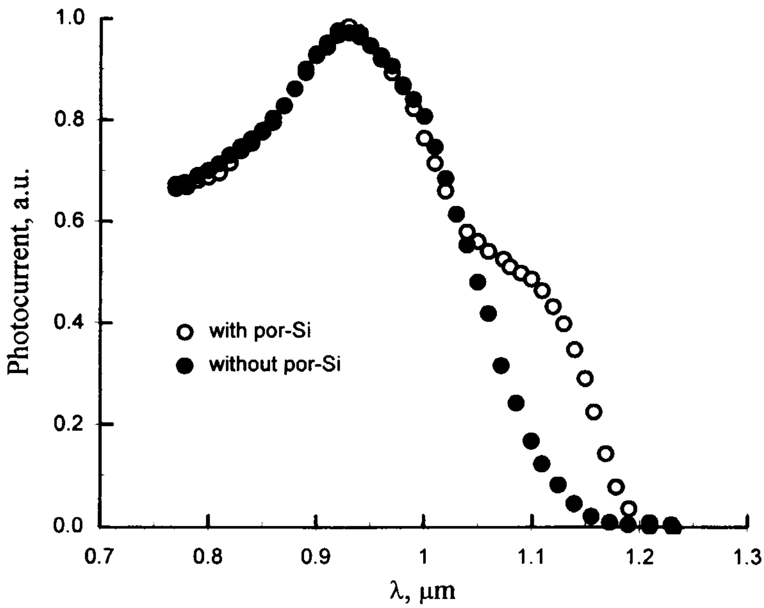

Fig. 11. Photoresponse spectra of silicon wafers without and with rear microporous layer (from Ref. [54]).

antireflecting coating indicates further decrease of losses for reflection with growth of por-Si thickness (Fig. 13). This anomalous effect, from the point of view of the authors of paper [58], is also caused by passivation of silicon surface by por-Si layer. In this case, possibly, the increasing serial resistance plays more important role. Nevertheless, the results obtained give the evidence of necessity of optimization of por-Si layer thickness when it is used as an antireflecting coating.

Besides the good antireflection properties confirmed experimentally, the por-Si film compared to other antireflecting coatings possess one more important advantage. Due to its porosity the film allows to obtain point contacts to the working layer of SC during evaporation of contact system onto its surface [44]. This, in turn, leads to decrease of contact resistance and recombination losses of photogenerated carriers in undercontact region of semiconductor. By simplicity of its technical realization, the aforecited method remarkably differs from methods of point contacts preparation in SC structures known at the present [59–60].

One more important aspect, which is necessary to consider while evaluating efficiency of usage of por-Si as an antireflecting coating, is compatibility of methods of porous layers formation with technology of manufacturing of silicon SC. In this respect it is necessary to note that it is preferable to form antireflecting porous layer before deposition of frontal contact system. However, such technological sequence is unacceptable for the contacts preparation by screen-printing. This is explained by the fact that, in the present case, good electrical contact with semiconductor's surface through the porous layer volume will not be

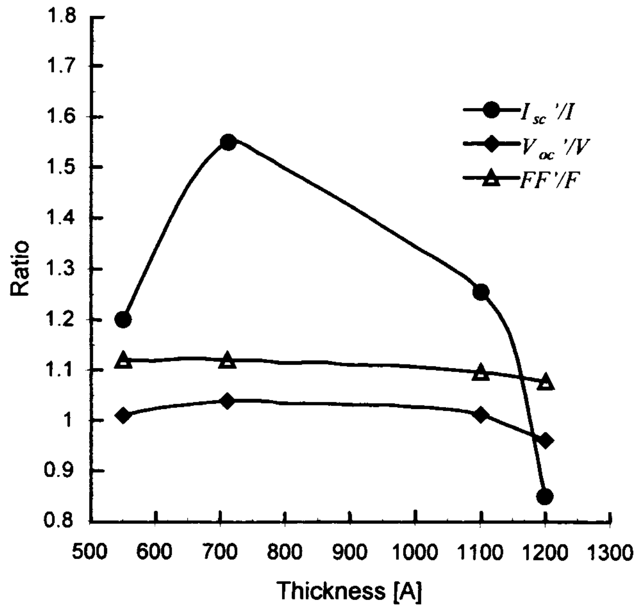

Fig. 12. The ratio of short circuit current (I_{sc}/I_{sc}), open circuit voltage (V_{oc}/V_{oc}) and filling factor (FF′/FF) as a function of por-Si layer thickness. I_{sc}, V_{oc}, FF and I_{sc}, FF—performances of silicon SC without and with por-Si layer respectively (from Ref. [58]).

ensured. At the same time, when the contacts are deposited before the por-Si layer formation on surface of SC structure, fingers of metal contact grid can be etched out in HF-based electrolyte.

This problem was solved in [6] by reduction of anodization time to 3–6 s and attainment of the necessary thickness of porous layer at the expense of increase of anodic current density. Such reduction of length of electrochemical processing has allowed to avoid considerable damage of the contact grid during formation of antireflecting porous layer on the final stage of the SC structure preparation.

3.2. *SC on por-Si/Si heterojunction base*

The first papers [7,27], which have proved a presence of quantum confinement effect of carriers in por-Si, have caused a huge interest not only creation opportunity a light-emitting devices on the basis of this material. The expansion of the por-Si bandgap caused by quantum size effect, is interesting and from the point of view of heterojunction Si-based SC creation. At that can be used a simple electrochemical etching of a silicon wafer. Research works, which have begun to be conducted in this field, had the spectral sensitivity range expansion of silicon SC by the purpose. It can be divided conditionally into 3 directions:

1. Use of a por-Si layer as the silicon SC emitter.

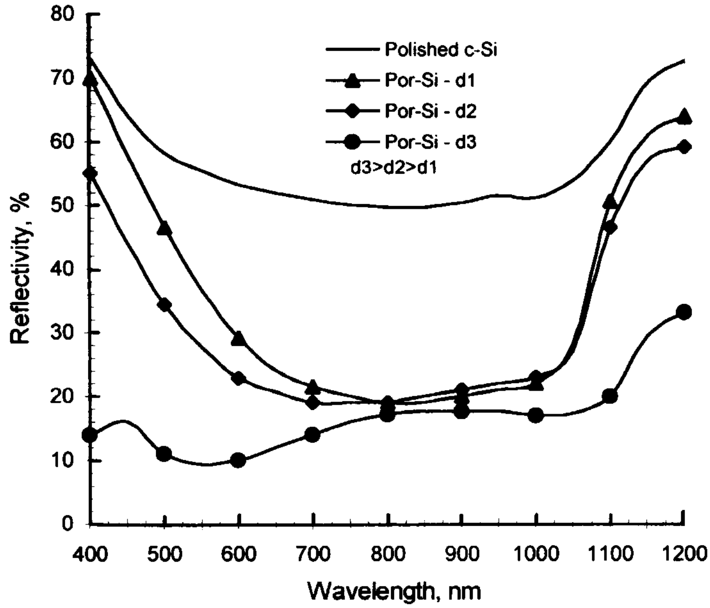

Fig. 13. Surface reflectance from different thicknesses of por-Si layers and polished c-Si (from Ref. [58]).

2. Creation of a tandem design SC with por-Si/n–Si/p-Si type structure.
3. Por-Si layer formation through diffusion p–n junction created in a substrate.

The most typical features of the first direction were inherent to SC structure, which was studied in paper [62]. To prepare it, a layer of por-Si was formed by electrochemical anodization of surface of silicon wafer with epitaxial p/p$^+$ junction. The epitaxial p-layer was 30 mm thick and had resistance 10 Ωcm, while the resistance of p$^+$-substrate was 0.001 Ωcm and was provided to assure good ohmic contact. Doping of the por-Si layer was realised by phosphorus diffusion at temperature 980°C over 15 min. The n-por-Si/p-Si/p$^+$-Si structure of SC obtained should, in the opinion of authors of paper [62], ensure optimised absorption of short wavelength radiation due to the use of por-Si as a window layer. However, they have obtained only 7% of photoconversion efficiency of this SC of 1×2 cm^2 area under AM 1 illumination.

Por-Si layer using for tandem design creation of silicon SC was investigated in papers [63–65]. Thus por-Si layer was formed by an electrochemical anodization on an emitter surface previously created the diffusion p–n junction. The por-Si/Si heterojunction, which arose in emitter volume, should ensure the optimized conversion of a high-energy part of a solar spectrum. It was confirmed by quantum efficiency measurements. However the series resistance of researched SC grows during porous layers formation. And it has become the limiting factor with high efficiency achievement [65].

The idea of accommodation of part of a por-Si layer in a space charge region volume of diffusion p–n junction was realized practically by Vitanov et al. [66]. For it the por-Si layer with thickness 1.5 μm was grown by electrochemical anodization on a structure surface with shallow n^+–p junction. As the n^+-region depth made less than 1 μm, porous layer has penetrated through n^+-p junction into p-type wafer. The received structure, in comparison with structure without por-Si, has shown a lower short-circuit current but had the increased photoresponse for light waves with length below 550 nm.

The por-Si/Si heterojunction electrical properties were investigated by Vitanov et al. in their subsequent paper [67] for an explanation of low photovoltaic properties of researched structures with a thick por-Si layer. It was determined by them, that in the mentioned structures the por-Si behaves as the intrinsic semiconductor, irrespective of initial dopant concentration in a substrate before its formation. Besides the carrier mobility in a heterojunction porous layer approximately one-fifth of its previous values than in a single-crystal substrate [67].

All opportunities of high-efficiency SC creation with a heterojunction on a por-Si basis were finally considered in paper [40]. After detailed studying of electrical and optical properties of Au/por-Si/Si/Au structures its authors came to a conclusion, that the photoelectric properties of a por-Si/Si heterojunction are determined largely by optical absorption in a single-crystal substrate. First of all it follows from the analysis of photovoltage spectra and photocurrent (Fig. 14), the low sensitivity to high-energy radiation absorbed in por-Si by which characteristics is. The ill-electrical characteristics of a porous layer by explanation of it can be. It

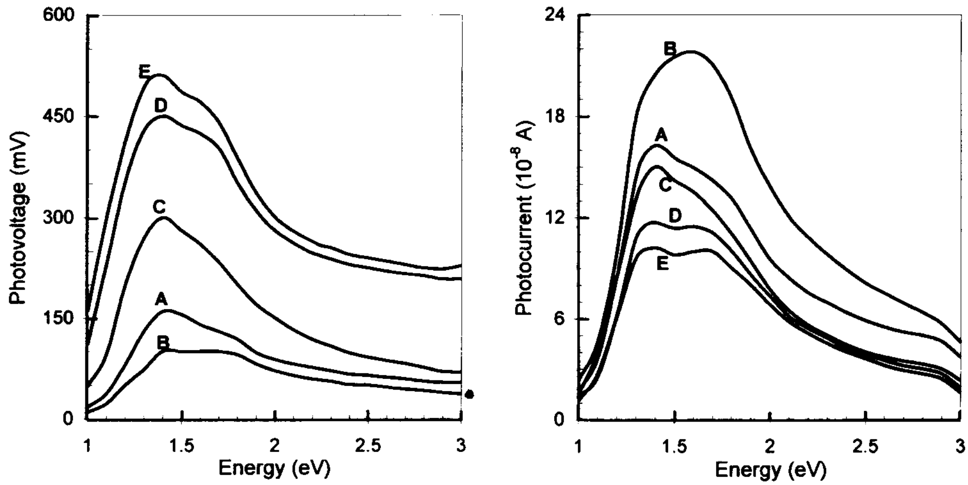

Fig. 14. Photovoltage and photocurrent spectra of different por-Si films. Film thickness (μm): **A**—5.6; **B**—9.1; **C**—16.3; **D**—24.7; **E**—30.0 (from Ref. [40]).

prevents the photogenerated carriers to pass in SCR and to diffuse to the suitable collecting electrode.

The improvement of photoelectric properties of structures with por-Si by a method of thickness increase of its layer is shown in paper [40] as unperspective. It, according to the carried out researches, will be inevitably accompanied by reduction of a photocurrent with insignificant increasing of an open-circuit voltage (Fig. 14) and can be explained by the increasing of series and shunting resistances of the same structures [40].

4. New directions of por-Si utilization in SC structures

4.1. Charge localized in the layer of partially oxidized por-Si

From the aforecited description of microstructure of por-Si, it follows, that thanks to the presence of developed system of pores, this material possesses considerably increased area of effective surface (according to various sources [1,68] from 200 to 600 m^2/cm^3). Its size can be controlled by change of thickness and porosity of the layer being formed. Thanks to this property, in volume of por-Si it is possible to accumulate a considerable amount of built-in positive charge, which appears during the partial low temperature oxidation of porous layer in dry

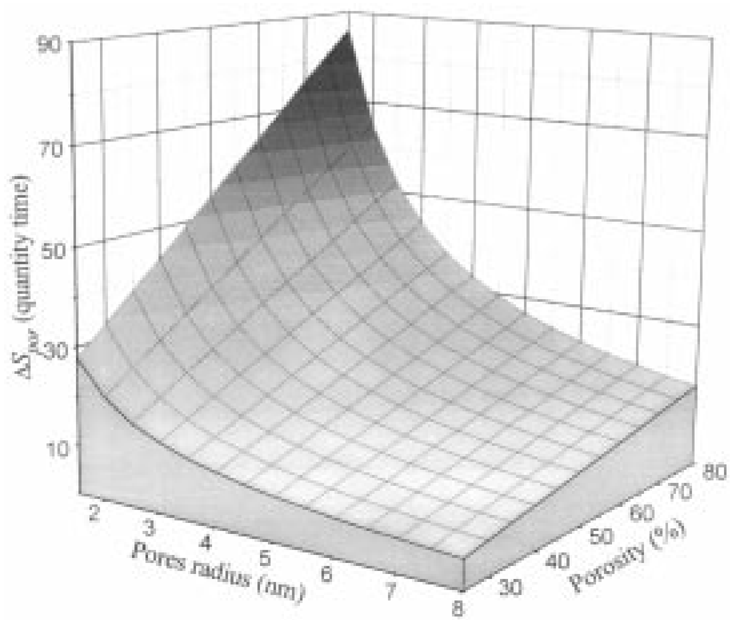

Fig. 15. Multiplicity of por-Si surface area increase (ΔS_{por}) as a function of pores radius and porosity of por-Si layer.

oxygen atmosphere. Thickness of oxide film formed here should be not less than 2.5–3 nm, because just in such near-surface region the positive charge fixed in SiO_2 is localized. Its creation is related to nonstoichiometry of transition layer of SiO_x ($0 < x < 2$) between single-crystal silicon and amorphous SiO_2 [69]. In respect to this it is fair to suppose, that in case of porosity of near-surface layer of semiconductor, density of built-in charge N_{ox} will increase proportionally to increase of frontal surface area of por-Si.

To determine magnification degree N_{ox}, it is necessary to calculate ratio of the effective surface area of por-Si layer S_{por} to area of original silicon plate S_{s} before its electrochemical anodization. As input data we will take S_{s} as well as the parameters of por-Si, which the technology of its preparation allow to reproduce with specified accuracy: thickness d, porosity C_{por} and pore radius r. On the principle that C_{por} in certain approximation represents by itself the ratio of area occupied by pores to area of frontal surface of silicon plate, one can easily determine the number of pores in idealized columnar structure of por-Si.

$$n = \frac{S_{\mathrm{s}} C_{\mathrm{por}}}{\pi r^2}. \tag{1}$$

When the thickness of por-Si layer is known, and in case of neglecting of pores expansion in its volume (is fully acceptable for the thickness up to several microns), the area of effective surface of porous film can be represented in the following form (Fig. 15):

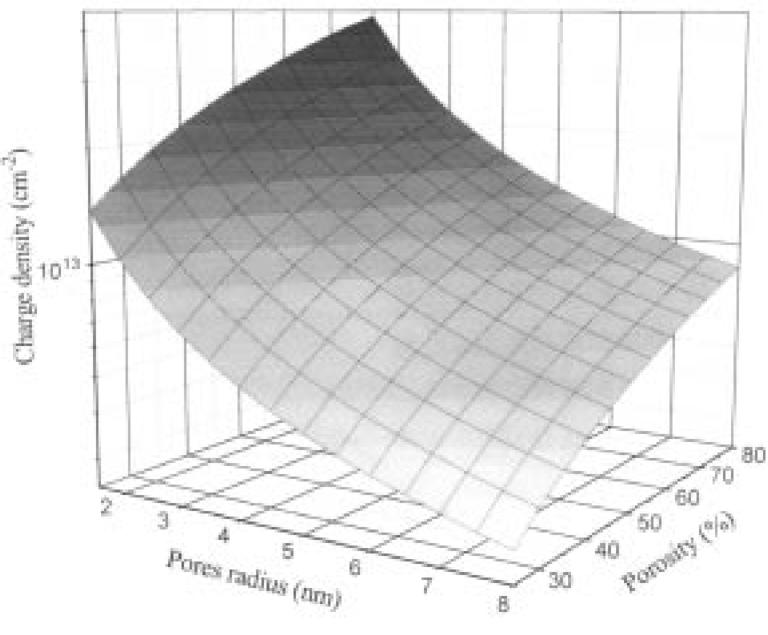

Fig. 16. Built-in charge density as a function of porous radius and porosity of por-Si layer.

$$S_{\mathrm{por}} = S_{\mathrm{s}} + \frac{S_{\mathrm{s}} C_{\mathrm{por}}}{\pi r^2} 2\pi r d = S_{\mathrm{s}} + \frac{2 S_{\mathrm{s}} C_{\mathrm{por}} d}{r}. \tag{2}$$

From analysis of the relation obtained it follows, that in the course of partial oxidation of the porous layer the density of positive charge localized in oxide, appearing during it, will increase proportionally to the increase of thickness and porosity of por-Si (Fig. 16):

$$N_{\mathrm{ox}} = N_0 \left(1 + \frac{2 C_{\mathrm{por}} d}{r} \right). \tag{3}$$

where N_0 is the density of the positive charge, fixed in oxide layer on Si planar surface.

The described method of creation of high density of the built-in charge in a frontal layer partially oxidized por-Si can be used for creation in near-surface region of SC semiconductor structure the sweeping electrical field. It will promote of a photogenerated carriers acceleration in a frontal layer in an n–p junction direction, reduction of their bulk and surface recombination velocity. The expedience of use of such sweeping fields near the frontal surface is proved by numerical modeling for a long [70]. Its efficiency cannot concede a back surface electric field that is widely used now. However, the practical realization of the sweeping field, built in a frontal layer, by creation of a necessary gradient of a dopant is connected to some technological difficulties. It is accompanied by lifetime reduction of the minority carrier and increase of a saturation current.

The increase of built-in SiO_2 charge carried by such way is perspective method of improvement of efficiency of SC with the structure Al/SiO_x/p-Si with induced inversion layer (MIS/IL) [71]. Physical p–n junction, appearing in substrate of p-type of such structure under the influence of positive charge localized in oxide layer, possesses the whole number of unique properties, which are important for the photoconversion process. As a result of this MIS/IL SC are potentially more effective than the SC with analogous diffusion p–n junction [72].

Essential imperfection of MIS/IL SC is high specific resistance of the induced inversion layer, which leads to considerable losses of generated power, and it can be decreased by increase of the built-in positive charge in insulator layer. However to reach its density higher than 5×10^{12} cm^{-2} is technological rather complex. This, in turn, actualizes the method of increase of built-in SiO_2 charge not at the expense of direct increase of its density, but by means of adding por-Si layer with considerably increased area of oxidized surface to the structure of MIS/IL SC.

4.2. SC efficiency increasing due to developed surface of p–n junction

The use of por-Si in structure of diffusion silicon SC can also assist to increase the photogeneration efficiency at the expense of the use of the porous microstructure of this material. Although the photocurrent of SC in general is defined by the number of electron-hole pairs separated by electric field of the SCR, it is evident, that in order to increase the efficiency of photoconversion it is

necessary to the limit to increase the volume of SCR. To reach this traditionally, at the expense of decrease of doping level of semiconductor, is beside the purpose, because such a step unavoidably will bring the increase of ohmic losses on serial resistance of the SC structure. More acceptable is the increase of the SCR volume, which can be reached by use of complex profile of p–n junction, being obtained in the course of diffusion of doping impurity through semiconductor surface with specified morphology. This, however, requires additional use of special mechanical or chemical treatment [73], which negatively influence the cost of the structures being obtained. At the same time, one can easily reach necessary effect on preparation of complex profile of p–n junction by diffusion of impurity through layer of por-Si [74]. During diffusion through the pores channels, for the depth exceeding the por-Si film thickness, and with correspondingly selected porosity, the p–n junction profile will tend to repetition of the porous layer surface profile (Fig. 17]. As a result of this, the SCR can reach the size of por-Si effective surface area, defined by means of relation (2) (Fig. 15).

However, it is necessary to note, that the diffusion through the layer of por-Si to obtain complex profile of p–n junction is connected with some technological difficulties related to microstructure and properties of this material. First, in the case, when diameter of pores equals to several units of nm, the passage of doping impurity molecules over their channels will be complicated. Secondly, developed surface of por-Si develops increased chemical activity of the porous layer. Because of this, the velocity of oxidation processes in por-Si considerably exceed the oxidation velocity of common Si. In the result, preparation of complex profile of p–n junction during doping by traditional diffusion methods in their specific

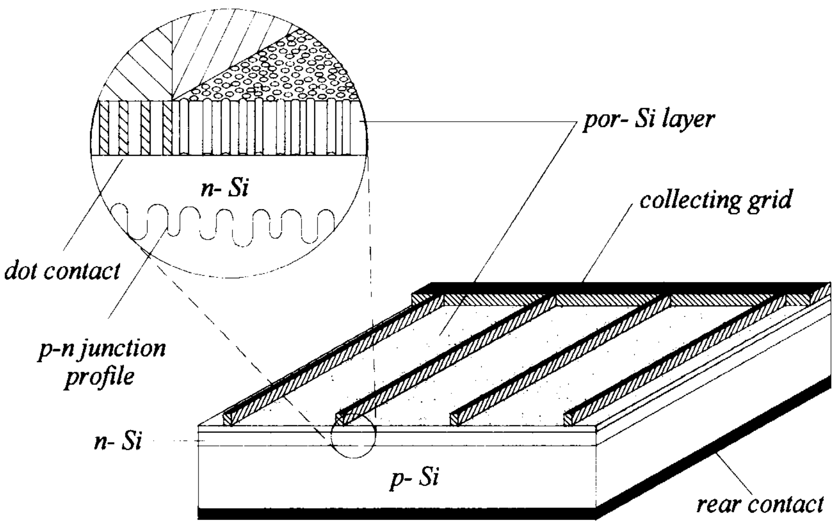

Fig. 17. Solar cell structure with frontal por-Si layer.

temperature range (1000–1100°C), becomes impossible due to closing of pores channels caused by oxidation of the por-Si, which proceeds in parallel to the diffusion.

The problem of diffusion of doping impurity through the pores channels can be solved by increase of the pores radius and also by decrease of the diffusion process temperature. If the first problem is solved by means of optimization of technology of por-Si layer formation, the decrease of temperature of doping requires to use low temperature sources of diffusion. The most suitable for this are specially developed for por-Si diffusants [74], which allow to carry doping at temperature near 850°C (Table 1).

With the objective of quantitative determination of the effect of the SCR area increase, we represent the value of maximal power, being generated by SC, as function of serial resistance R_s, saturation current I_s and photocurrent I_L [75]:

$$P_m = \left(\frac{nkT}{q}\right) I_L(1-\gamma)\ \ln\left(\gamma \frac{I_L}{I_s}\right) - R_s I_L^2 (1-\gamma)^2. \tag{4}$$

Considering that I_s and I_L are the values, depending on area of p–n junction, and efficiency of SC is represented in form of ratio of P_m to power of the incident light flux P_{in}, we will obtain relation, which connect η and the area of the p–n junction A:

$$\eta = \frac{A\left[\frac{nkT}{q} J_L(1-\gamma)\ \ln\left(\gamma \frac{J_L}{J_s}\right) - R_s J_L^2 A (1-\gamma)^2\right]}{P_{in}}, \tag{5}$$

Table 1
Solid planar sources for boron and phosphorus diffusions in por-Si volume

Basis materials of sources	Deposition temperature (°C)	Average sheet resistance (Ω/sq), deposition time (min)		
		10	30	50
LaP_5O_{14}	800	280	104	95
	850	120	54	40
	925	22	13.7	10.3
SiP_2O_7	850	–	1290	720
	900	255	56	38
	950	42	18.5	12.7
$Al(PO_3)_3$	950	95	33	20
	1000	26	11.4	7.7
	1100	4.8	3.1	2.5
ABSG	850	840	210	120
	1000	34	22	18
	1100	4.0	2.8	2.2

where

$$\gamma = \left[1 + \frac{\ln\left(\gamma \dfrac{J_L}{J_s}\right)}{1 + 2R_s J_L A \gamma \left(\dfrac{q}{nkT}\right)} \right]^{-1};$$

J_L and J_s are the density of photocurrent and saturation current respectively.

The results of calculations, carried according to Eq. (5), presented in Fig. 18 and are the demonstrative confirmation of the effectiveness of use of por-Si for increase of area of SCR and correspondent increase of efficiency of SC.

4.3. Por-Si photoluminescence for photoconversion efficiency increasing

Despite multiple experimental works, carried during seven years in field of study of photoluminescence of por-Si in visible spectral range, the physical nature of this optical phenomenon still remains unclear [9]. Presently, some basic models are proposed, which relate appearance of intensive photoluminescence in por-Si with:

1. Broadening of band gap and radiative optical transitions in nanometric silicon crystallites of quantum wires (quantum size effect) [7].
2. Formation of amorphous silicon phase (α-Si:H) [76], luminescent chemical

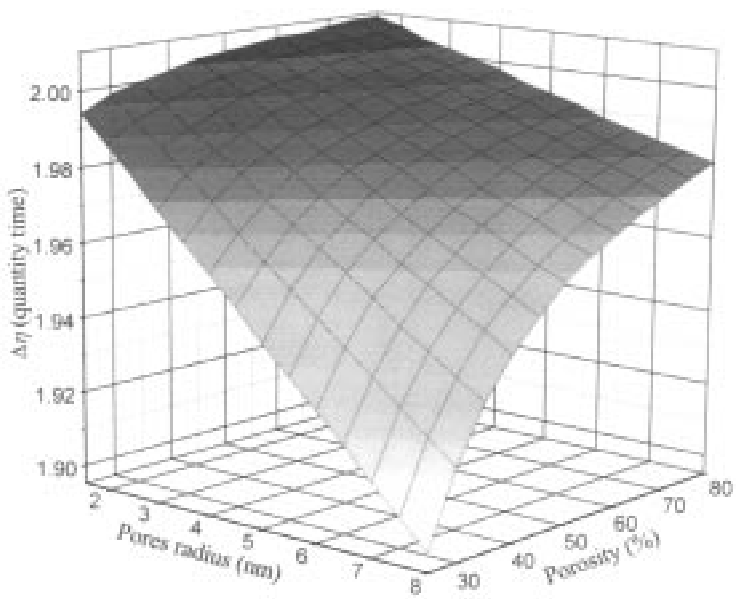

Fig. 18. Increase of solar cell efficiency as a function of pores radius and porosity of frontal por-Si layer.

compound of siloxene type ($Si_5O_3H_6$) [77] or silicon hydride (SiH_x [78] on the por-Si surface during the course of electrochemical etching of Si.
3. Radiative recombination of charge carriers through the surface states of quantum size objects [79], defects in silicon or in oxide layer on its surface [80].

The photoluminescence spectra perse, wide and structureless by their shape, as well as variation of the luminescence characteristics subject to conditions of por-Si preparation and treatment of its surface, did not give decisive arguments in favor of none of the models cited above. The discussion concerning an origin of visible light emitting from por-Si proceeds. However, the majority of an existing experimental material will be coordinated with the quantum confinement theory [9].

Ambiguity of interpretation takes place also during discussion of mechanisms of excitation of por-Si photoluminescence. Two main points of view are known on that matter. The first one relates photoluminescence excitation with light absorption in the same objects, in which it is observed [81,82]. The second point of view supposes that the exciting light absorption and luminescence can be related to different objects. Here, the transfer of excitation from the 'absorption centers' to 'radiation centers' takes place [83].

Despite some indefiniteness in sense of clarification of nature of photoinduced light emission from por-Si, the use of this optical phenomenon in the process of

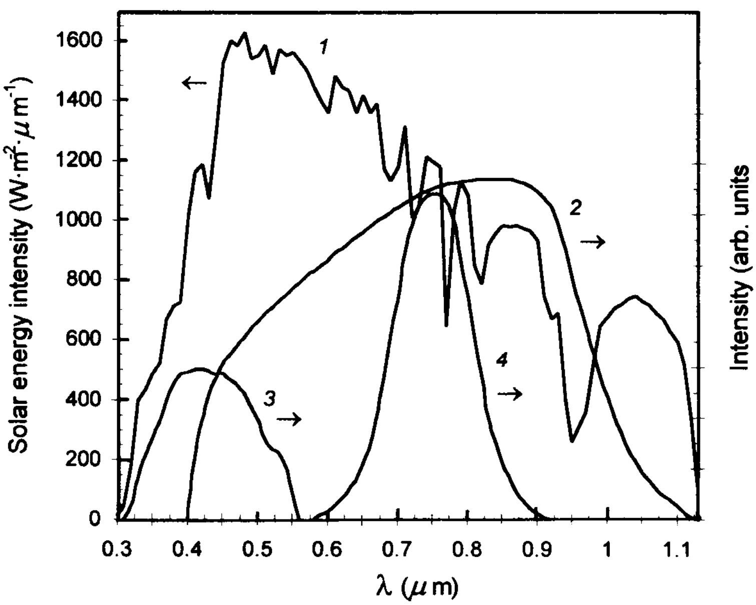

Fig. 19. Spectra of solar energy intensity (1), silicon solar cells sensitivity (2), photoluminescence excitation (3) and photoluminescence (4) of por-Si layers.

photovoltaic conversion in structure of silicon SC can assist their efficiency increasing [74].

According to the studies of excitation spectra [81,82,84], strong photoluminescence is observed during absorption of photons with energy in range 0.3–0.55 microns by por-Si (Fig. 19(3)). The band of intensive luminescent emission here comprises about 250–300 nm (Fig. 19(4), and its maximum subject to conditions of electrochemical processing and parameters of original material can be located in the range from 530 to 850 nm (see, for example, [85,86]). Owing to this, the possibility of effective absorption of part of solar radiation violet component as well as its reemission in range of maximal spectral sensitivity of silicon SC (Fig. 19) appears. Thus, inclusion of luminescent layers of por-Si in structure of silicon SC will assist the decrease of photoconversion losses, connected with:

1. Terminalization of hot carriers (during absorption of high energy light quantum by SC structure and formation of electron-hole pair, the excess of its energy ($h\nu$-E_g) is transferred to semiconductor crystal lattice of oscillations assisting to heating of SC, and finally, decrease of its open circuit voltage ~2 mV/K) and efficiency (~0.05% K)).
2. Limited spectral sensitivity of silicon SC in short wavelength range of solar light, which quanta, as a result of high absorption coefficient, generate

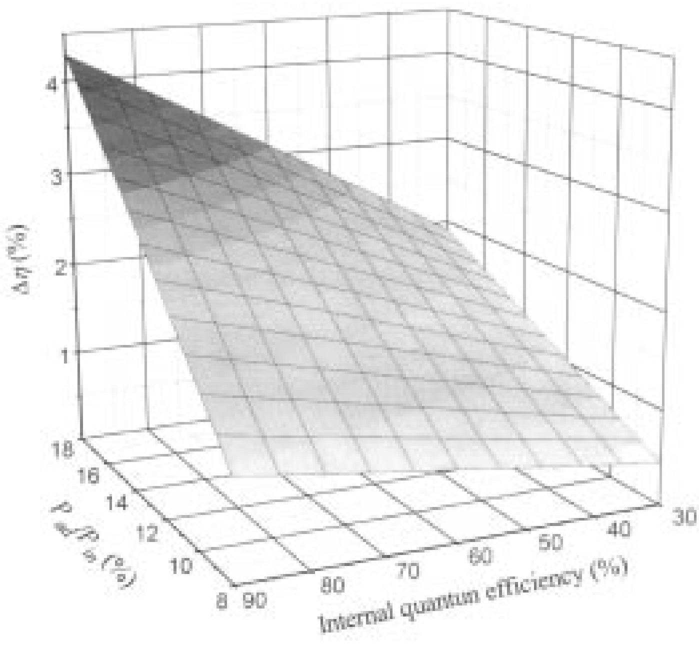

Fig. 20. Increase of solar cell efficiency as a function of internal quantum efficiency of por-Si photoluminescence and share of the reradiated light flow.

nonequilibrium carriers in thin near surface region of SC structure, what due to the surface recombination influence does not permit them to make their input in photocurrent.
3. By the use of special selectively absorbing coatings, which, in order to eliminate the losses mentioned in (1) and (2), reflect light quanta of ultra violet range from the SC surface, reducing by that the flux of absorbed solar energy not less than by 20%, and limiting by that the efficiency of photoconversion in silicon SC.

The formula (5) can be used for calculation of the efficiency increment of SC ($\Delta\eta$), when they absorb additional light flux P_{ad} at the cost of reemittance of part of ultraviolet component of solar spectrum by por-Si in more optimal for operation of silicon SC spectral range. In this the photocurrent density J_L should be expressed as the function of P_{ad} and difference of internal Q_{in} and external Q_{ex} quantum efficiency of photoluminescence:

$$J_L = P_{ad}(Q_{ex} - Q_{in}). \tag{6}$$

This approximation will be valid under condition, that the depth of p–n junction is conformed with maximum of photoluminescence spectrum of por-Si, and the majority of nonequilibrium carriers of charge are generated by reemitted quanta in SCR. Assuming, that the value of Q_{ex} can reach 10% according to [10], and P_{ad} depending on width and spectral position of the photoluminescence excitation spectrum can be changed from 8 to 18% of the incident light flux power, the efficiency of photoconversion of silicon SC can additionally be increased by 0.5–4% (Fig. 20). Therefore, the calculated data presented confirm the assumption, that the use of por-Si layer in structure of SC will help to reach two incompatible objectives—the operating range expansion into ultraviolet spectral range and simultaneous decrease of heating losses connected with it.

5. Summary

Generalizing the existing practice of photovoltaic use of por-Si, first of all it is necessary to note the reasons of certain unsuccessful experiments on improvement of silicon SC efficiency, when por-Si is included in its structure. First of all, attempts to fabricate wide band window of heterojunction on the base of por-Si [62] were fated to failure due to high specific resistance of the porous layer and low efficiency of photogenerated carriers collection in it [40,41]. For the same reason, the recombination losses on serial resistance did not allow to reach high-efficiency of photoconversion in SC, which emitter was combination of layers of porous and single-crystal silicon [63–65]. Secondly, the use of por-Si layers as antireflecting coating of silicon SC cannot give the expected effect of efficiency increasing [53,58], if the thickness of the porous layer is not optimized. The decrease of photocurrent of por-Si antireflected SC with simultaneous reduction of

their reflection losses with increase of the porous layer thickness observed in paper [58] is its demonstrative confirmation.

Now we shall stop on the most essential achievement in the field of por-Si using in silicon SC structures. On the present moment its concern only to antireflecting coatings on this material base:

1. Such antireflecting coating of the single-crystal silicon surface by the por-Si optimized layer allows to reduce losses on optical reflection from 1.6 to 3.4% in a spectral range from 400 to 900 nm [43] and on efficiency is compared only to an antireflecting coating on MgF_2/ZnS base put on a previously texturized silicon surface [1].
2. The integrated reflection coefficient of a polycrystalline wafer surface, where por-Si layer is generated, makes 4.7–4.9% for light waves with length from 350 to 1120 nm [1] and leaves behind the previous record (6.6% in a range 500–1000 nm). It was achieved with the mechanical structuring of a surface [87].

As to the prime cost and technological simplicity of the antireflective coatings for the silicon SC, the por-Si in this respect is the leader as well. This is the most important for polycrystalline SC, for which minimization of reflection by the surface texturing by means of cheap anisoptropic chemical etching is inefficient due to chaotic orientation of grain. At the same time, more efficient methods of mechanical or laser structuring of surface do not make cheaper the technology of SC structure fabrication.

The method of surface texturing of silicon surface by formation of thick layers of por-Si on it is not less promising from point of view of photovoltaic use. In the case, when the dimension of inhomogeneities of porous layer is proportional to the light wavelength, such microporous layer can assist to capture and detention of light quanta in SC structure. Owing to multiple increase of optical path of infrared range quanta, it is possible to increase quantum efficiency in region of band edge absorption of single-crystal silicon, increasing by that the efficiency of SC. First experimental confirmations of spectral sensitivity expansion of silicon SC with thick microporous layers of por-Si were obtained in papers [54,57]. Due to simplicity of technological realization, the use of such method of the surface texturing can be more efficient, than the method of anisotropic etching used presently in technology of silicon SC [88].

If by the present time the efficiency of use of por-Si as antireflecting coating for silicon SC is confirmed by a number of experimental papers [1,43,46,52,53,58,61], its passivating properties still require detailed study. Nevertheless, the experimental results fixed in [46,50,52–54], give the evidence of correlation of the SC efficiency increase not only with the antireflection, but also with passivating influence of por-Si frontal layer. The most frequently this is related to the hydrogen coating of por-Si surface occurring during the process of the porous layer formation. It is theoretically justified in paper [1], where it is shown that hydrogen passivation can reduce the surface recombination velocity up to the level of 1 cm/s. This is lower almost by two orders than the surface recombination velocity typical for silicon surface passivated by thermal oxide. Transient

photoconductivity measurements carried out in paper [54] clearly indicate the decrease of surface recombination velocity under passivation of silicon surface by layer of por-Si. Therefore, possibly in the near future, the por-Si will be considered as alternative for passivating coatings from silicon dioxide and nitride, used today in high-efficiency silicon SC [88,89].

Despite the positive experimental results, obtained in the use of por-Si as optical and passivating coating for silicon SC, it is not necessary to limit its photovoltaic application by the borders of this region only. As the aforecited results of numerical calculations show, perspective directions of the use of por-Si for improvement of photoconversion efficiency in silicon SC are also [90]:

1. The increase of density of built-in SiO_2 positive charge by low temperature oxidation of por-Si in dry atmosphere of O_2/N_2. The increased area of its effective surface caused by porous structure of this material (Fig. 15) will assist the increase of built-in charge value proportionally to the surface area of the porous layer (Fig. 16). This property of por-Si can be used for the built-in electric field creation in the near surface region of SC structure, which will promote increase of collection efficiency of photogenerated carriers in SC with different type of structures.
2. The increase of internal quantum efficiency of silicon SC at the cost of increase of the SCR volume during creation of developed surface of p–n junction in the process of diffusion of doping impurity through the pores channels of por-Si. The increase of photocurrent conditioned by that is proportional to the p–n junction area and promotes considerable increase of the SC efficiency (Fig. 18).
3. The expansion of operating spectral range of silicon SC in ultraviolet region of the spectrum with simultaneous reduction of heat losses due to reemission by the por-Si layer of high energy photons in region of maximal spectral sensitivity of silicon SC. Depending on the value of internal quantum efficiency of luminescence of por-Si, silicon SC can additionally absorb part of violet component of solar light, and the increase of their efficiency in this can be up to 4% (Fig. 20).

Insufficient amount of experimental material, as well as certain technological peculiarities, do not allow presently to confirm completely the effectiveness of the aforecited directions. However, the number of studies in the field of photovoltaic use of por-Si constantly grow and quite possibly, in the near future, the layers of this material will be the integral part of the high-efficiency silicon SC structures.

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